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## GLASS FOR OBTAINING RIGID OPTIC FIBERS

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The effect of rare-earth oxides ( $\text{WO}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ) on technological and physical-chemical characteristics of optical glasses for light-guiding fiber cores is investigated. Glass compositions for optical glass fiber which satisfy the main requirements imposed on them are synthesized. The glass compositions indicated can be used to produce fiber-optic articles.

**Key words:** optical glass, synthesis, glass fiber, physical-chemical properties, light guide.

A rigid optical fiber consists of a light-guiding fiber core and two claddings.

The glasses used for the light-guiding core (TBF-10) and the light-reflecting cladding (VO-50), which are currently used in production, do not meet all requirements for obtaining fiber-optic articles, specifically, twistors (turners). For example, surface crystallization of the TBF-10 glass is observed in the temperature range 800–1150°C with the main phases precipitating  $\text{LaTiO}_3$ ,  $\text{Ba}_2\text{LaZrO}_{5.5}$ , and  $\text{La}(\text{B}_{0.95}\text{SiO}_{4.93})$ . In addition, the glass formulation contains class-I hazard oxides ( $\text{CdO}$  and  $\text{As}_2\text{O}_3$ ); a considerable difference is observed in the linear thermal expansion coefficient (CLTE) between the glasses TBF-10 and VO-50 —  $77 \times 10^{-7}$  and  $55 \times 10^{-7} \text{ K}^{-1}$ , respectively; the viscosity characteristics of the glasses do not match in the temperature range 600–1100°C. For VTO-73 glass used for protective cladding, diffusion of coloring impurities into the light-guiding fiber core is observed. These drawbacks limit the possibility of obtaining high-quality rigid optical fiber and fiber-optic articles based on it.

A twister is a fiber-optic element used in electro-optical systems for turning an image by 180°. The technology for obtaining twistors requires that the thickness of the light-reflecting cladding be increased, since as a result of a number of operations performed at the time the fiber-optic article is manufactured it becomes thinner and is stretched. Increasing the dimensions of cladding when there is a substantial discrepancy between the CLTE of the TBF-10 and VO-50 glasses results in the appearance of fine cracks at the “light-guiding fiber core – cladding” interface, which gives rise to a series of dark spots on the area of the plate. The

main, crucial technological operation in obtaining twistors is turning one surface of the blank relative to the opposite surface by 180°, which is done at 650–660°C. In this region the cladding glass already is in a plastic state ( $\log \eta \approx 9$ ), while the glass for the light-guiding fiber-core is brittle ( $\log \eta \approx 13$ ). For this reason, when the surface of the fiber-optic plate is turned the light guides at its center become deformed, which in turn presupposes that they are shifted from their initial position and the total decrease of light transmission by the article decreases.

This makes it necessary to optimize the compositions of the glasses for a light-guiding fiber core and the light-reflecting cladding with respect to a complex of technological and physical-chemical characteristics.

To solve this problem a series of glasses was synthesized on the basis of the system  $\text{BaO} - \text{La}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2 - \text{TiO}_2 - \text{ZrO}_2 - \text{Nb}_2\text{O}_5$ , in which the sum of oxides  $\text{B}_2\text{O}_3 + \text{ZrO}_2 + \text{SiO}_2 + \text{Nb}_2\text{O}_5$  was constant and equal to 60%<sup>2</sup> (Fig. 1).

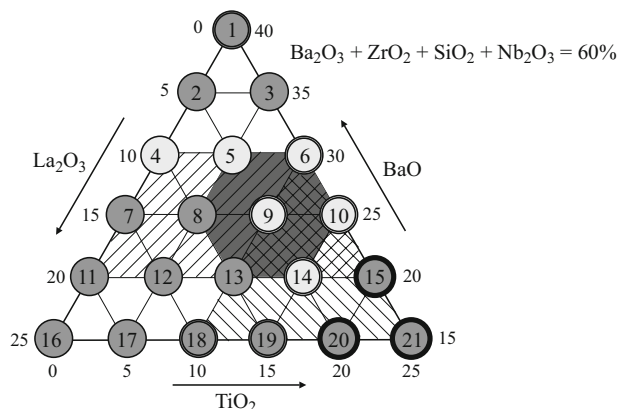
The choice of system depends on the requirements that need the glasses possess refractive index not less than 1.77, CLTE in the range  $(70 - 80) \times 10^{-7} \text{ K}^{-1}$ , and a short formation interval.

The results of six-hour heat-treatment established that the maximum degree of crystallization of the experimental glasses appears at high titanium oxide concentrations 15–25%. The EPR data showed that there are no variable valence ions (in this case  $\text{Ti}^{3+}$ ) in the glass, and the crystallization of the experimental glasses is due to the formation of  $\text{TiO}_2$  crystals (white enamel-like color).

Because borosilicate glasses assimilate  $\text{La}_2\text{O}_3$  well its introduction has a positive effect up to content 10%. Increasing

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<sup>2</sup> Here and below, unless otherwise state, the molar content, %.



**Fig. 1.** Compositions of the experimental glasses, their crystallization power, and the boundaries of the regions of the main indicators where the requirements for glasses to be used for light-guiding fiber cores meet all requirements: ○) glass crystallizing during founding; ○) opacified glasses; ○) glasses without visible indications of crystallization; ●) volume crystallization during heat treatment; ○) surface crystallization during heat treatment; glass composition ranges: (▨) index of refraction  $> 1.77$ ; (▧) possessing the required production quality range; (■) CLTE  $(70 - 80) \times 10^{-7} \text{ K}^{-1}$ .

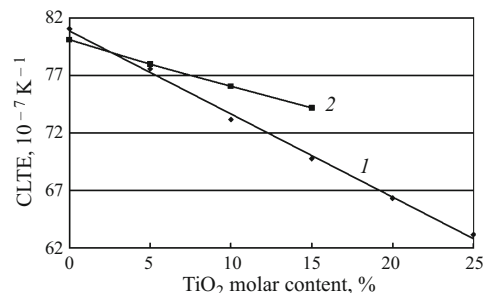
the amount of  $\text{La}_2\text{O}_3$  above 10% stimulates the appearance of intense volume crystallization of the experimental glasses with lanthanum-containing phases precipitating as the main products of crystallization and it increases the formation temperature range. The minimum degree of phase separation is characteristic for glasses in which the  $\text{TiO}_2$  content is 9–11% and the  $\text{La}_2\text{O}_3$  content is 8–10%.

One of the main characteristics of the a rigid optical fiber is the numerical aperture, which characterizes the fiber's capability to collect light rays and is determined by the value of the refractive index of the light-guiding fiber core and of the light-reflecting cladding. To ensure the required transmission of light rays incident at a large angle to the optical axis and to create the required frequency-contrast characteristic of the fiber article its aperture number must be  $A > 1$  [1].

Glass for the light-guiding fiber core of a rigid optical fiber is characterized by low  $\text{SiO}_2$  content, which is 25–35% and contains mainly heavy metal oxides ( $\text{TiO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and others), making it possible to reach refractive indices 1.7–1.9. High values of the refractive index are obtained by adding titanium and lanthanum oxides, and minimal values are obtained by added silicon and boron oxides.

The refractive index of the experimental glasses was determined by the immersion method and by L. I. Demkina's computational method [2].

The CLTE plays an important role in the fabrication of light guides. To obtain a rigid optical fiber with the required thermo-mechanical strength the CLTE of the glass for light-reflecting cladding must be somewhat less than the CLTE of the glass of the light-guiding fiber core. According to published data [3], the optimal difference of the CLTE between the core and cladding for glasses of a rigid optical fi-



**Fig. 2.** The CLTE of the experimental glasses for the light-guiding fiber core versus the  $\text{TiO}_2$  content: 1, 2) molar content of  $\text{BaO}$  15 and 25%, respectively.

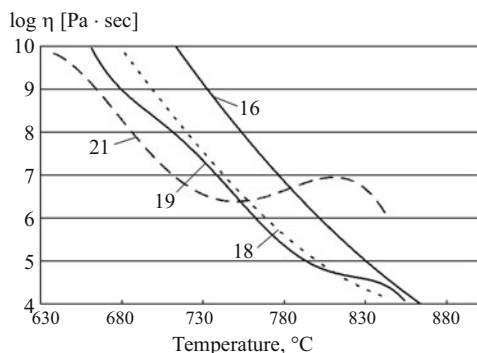
ber lies in the range  $(5 - 12) \times 10^{-7} \text{ K}^{-1}$ ; this is due to the need to create compression stresses in the cladding of the rigid fiber. In the system under study the CLTE of the experimental glasses varies over the range  $(63 - 84) \times 10^{-7} \text{ K}^{-1}$  (Fig. 2).

It was determined that the composition range of the glasses with the required CLTE is limited as follows (5): 20–30  $\text{BaO}$ , 5–15  $\text{TiO}_2$ , 0–10  $\text{La}_2\text{O}_3$ .

To ensure high-quality drawing of a rigid fiber made of three glasses with different compositions the viscosity of the glasses in the core and cladding must match over a wide temperature range [4]. When new glass compositions are developed for light-guided fiber cores of rigid optical fibers the main problem is that the indicated glass must be “short.” The term “short” means glass characterized by viscosity variation  $10^{10} - 10^4 \text{ Pa} \cdot \text{sec}$  in a narrow temperature range  $\Delta t = 100 - 170^\circ\text{C}$ . If the glass does not meet this requirement, the drawing regime must be adjusted (temperature, drawing velocity, cladding thickness), as a result of which the optical fiber acquires different characteristics (fiber diameter, cladding thickness, light-guide diameter), which in turn affects the volume of the information transmitted.

In most cases the viscosity is determined either in the region of the transition into the glassy state ( $10^{12} - 10^8 \text{ Pa} \cdot \text{sec}$ ) or in the region of the melt ( $< 10^5 \text{ Pa} \cdot \text{sec}$ ). The data are very sparse for the intermediate region  $10^8 - 10^5 \text{ Pa} \cdot \text{sec}$ , so that it is urgent study the viscosity of glass in the interval  $10^{10} - 10^4 \text{ Pa} \cdot \text{sec}$ , determining the measure of the glass “length.” In the present work it was determined by compressing a continuous cylinder using a PPV-1000 viscosimeter manufactured by Orton (USA).

Figure 3 shows the dependence of the temperature variation of the viscosity on the titanium oxide content. As one can see from the figure, titanium oxide additions to the experimental glasses shift the viscosity curve into the low-temperature region, and increasing the content of the oxide  $\text{La}_2\text{O}_3$  has the opposite effect. These temperature dependences of the viscosity show that for the experimental glass composition No. 21 the viscosity increases appreciably when the sample is heated uniformly. This fact shows that these glasses are prone to phase separation (volume crystalliza-



**Fig. 3.** Logarithm of the viscosity of the experimental glasses versus the temperature: 16, 18, 19, 21) numbers of the compositions (in accordance with Fig. 1) of the experimental glasses for the light-guiding fiber core of a rigid optical fiber.

tion). A considerable growth of the viscosity with constant and continuous increase of the temperature indicates the appearance of the first crystals in the volume of the glass, which begin to dissolve when a prescribed temperature is reached, and the viscosity of the experimental glass decreases.

Thus, titanium oxide does not play a unique role in glasses for a light-guiding fiber core: on the one hand by increasing its concentration it is possible to obtain glass with a high index of refraction and a short formation interval, but on the other hand it stimulates the appearance of phase separation — liquation and crystallization.

Studies have determined a glass composition with minimal phase separation and with the refractive indices and CLTE within the required limits. At the same time the temperature variation of the viscosity curve in the range  $10^{10} - 10^4$  Pa · sec for the indicated glass is shifted to high temperatures, which does not correspond to the requirements that glass to be used in fiber optics must meet.

To predict the precipitation of the crystalline phases indicated for TF-10 glass and to adjust the viscosity characteristics on the basis of the optimal composition of the glass, four independent series of glass were synthesized. The following partial replacement of oxides with step 1% was made: BaO — with 1 – 5% calcium oxide (Ca series); SiO<sub>2</sub> — with 1 – 6% tungsten oxide (W series); La<sub>2</sub>O<sub>3</sub> — with gadolinium oxide (Gd series) and La<sub>2</sub>O<sub>3</sub> — with 1 – 6 % yttrium oxide (Y series).

Using calcium oxide (Ca series) permits increasing negligibly the coefficient of dispersion (from 42.32 to 42.37) and at the same time decrease the index of refraction (from 1.7797 to 1.7719) and the average dispersion (from 0.018422 to 0.018218), which is due to the close values of the partial coefficients for barium and calcium oxides. In addition, CaO additions lower the CLTE of the experimental glasses from  $78.4 \times 10^{-7}$  to  $77.5 \times 10^{-7}$  K<sup>-1</sup>. Increasing the calcium oxide content in the glass above 3% does not substantially diminish crystallization, so that its introduction above the indi-

cated amount is unjustified for the series being studied. This adjustment prevents the appearance of surface crystallization right up to its vanishing in the formation temperature interval 850 – 1000°C, but at the same time eliminates the possibility of obtaining glass of the “short” type, which limits the use of the indicated composition under production conditions.

Tungsten oxide additions in series W optical glasses increase the refractive index from 1.78165 to 1.82525, decrease the temperature variation of the viscosity curve, shifting it to low temperatures; this is due to the fluxing power of WO<sub>3</sub>, which lowers the viscosity of glasses, forming log-melting compounds — tungstenates [5]. The CLTE remains at the same level. However, the use of WO<sub>3</sub> in optical glasses of the system BaO – La<sub>2</sub>O<sub>3</sub> – B<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> – TiO<sub>2</sub> – ZrO<sub>2</sub> – Nb<sub>2</sub>O<sub>5</sub> is limited: in amounts above 3% it results in volume crystallization even with heat treatment for 2 h. Thus by adding 1 – 3% WO<sub>3</sub> the degree of crystallization of the optical glasses can be lowered while maintaining prescribed viscosity characteristics.

Further adjustment of the compositions was done in the direction of using Gd<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>. This is because lanthanum, yttrium, and gadolinium oxides are rare-earth oxides with the general formula R<sub>2</sub>O<sub>3</sub>. The reactivity of lanthanide atoms and the substantial similarity of their chemical properties are directly related with their structure; this is due to the fact that the number of electrons in the two outer shells is the same:  $4d5s^2$  — for yttrium,  $5d6s^2$  — for lanthanum,  $5d6s^2$  — for gadolinium [6].

It was established in the course of the studies that when Gd<sub>2</sub>O<sub>3</sub> is used in the experimental glasses the level of the optical properties decreases (index of refraction, average dispersion, coefficient of dispersion) and therefore the numerical value of the aperture. Additions of this oxide in the amounts 1 – 3% to the Gd series experimental glasses stimulate volume crystallization even with four-hour heat treatment, which limits its use in this system. At the same time, increasing the Gd<sub>2</sub>O<sub>3</sub> amount to 3 – 6% decreases the glass formation interval and shifts the temperature dependence of the viscosity to low temperatures.

Series Y glasses containing 1 – 3% yttrium oxide are characterized by the required degree of melt uniformity, absence of striae, and comparatively low founding temperatures (1250 – 1260°C). It should be noted that Y<sub>2</sub>O<sub>3</sub> decreases the optical properties negligibly, which is due to the close values of the partial coefficients of Y<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> for the refractive index, the average dispersion, and Abbe number.

In the amount 3% in BaO – La<sub>2</sub>O<sub>3</sub> – B<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> – TiO<sub>2</sub> – ZrO<sub>2</sub> – Nb<sub>2</sub>O<sub>5</sub> glasses Y<sub>2</sub>O<sub>3</sub> imparts total stability with respect to crystallization with three-hour heat treatment. However, when the soaking time increases to six hours surface crystallization is observed in the temperature interval 980 – 1000°C. Yttrium oxide should not be used in amounts greater than 3%, since similarly to lanthanum oxide Y<sub>2</sub>O<sub>3</sub> limits the possibility of obtaining “short” glass, a limitation that is undesirable for drawing rigid optical glass fiber.

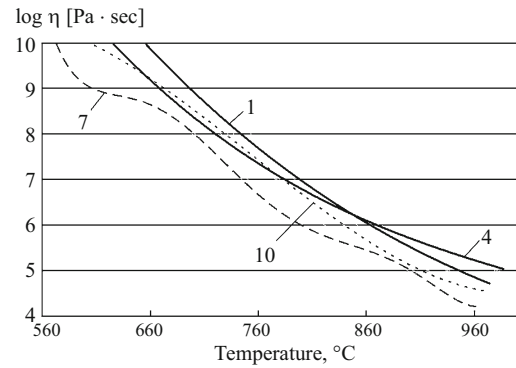
According to the studies the optimal results were obtained for series W and Y glasses. In the first case it is possible to synthesize glass with a short output interval and high optical properties while Y series glass is highly stable with respect to phase separation. To determine the combined effect of yttrium and tungsten oxides on the complex of technological and physical-chemical characteristics a series of XY glasses, where the tungsten oxide content was varied in the range 1 – 3% with  $Y_2O_3$  content held constant at 3%, was synthesized. It was determined that the use of  $Y_2O_3$  and  $WO_3$  in this series of glasses permits lowering the crystallization to vanishing. The low-temperature viscosity decreases and the high-temperature viscosity increases, which makes the glass “short” and permits using it for the light-guiding fiber core of a rigid optical fiber. The optimal composition of WY1 glass was determined from the results of the work. Table 1 compares the properties of commercial TBF-10 glass and the synthesized WY1 glass.

According Table 1 the physical-chemical properties of TBF-10 and WY1 glasses are essentially identical, which shows the real possibility of using this composition to produce the light-guiding fiber core of a rigid optical glass fiber.

The improvement of the commercial composition of TBF-10 glass has changed its formation temperature range, which made it necessary to adjust the commercial composition of VO-50 glass not only with respect optical and thermal but also rheological properties.

In this connection a series of experimental glasses was synthesized for a light-reflecting cladding based on the system  $K_2O - B_2O_3 - SiO_2$ , limited by the content of oxides (%): 65 – 80  $SiO_2$ , 15 – 30  $B_2O_3$ , and 5 – 20  $K_2O$ . Glass used for the light-reflecting cladding is characterized by a low index of refraction ( $n_D = 1.45 - 1.48$ ) as required for attaining aperture  $A > 1$ ; CLTE that differs from CLTE of the light-guiding core by  $(5 - 12) \times 10^{-7} K^{-1}$ ; and, a wide output interval, which is a mandatory condition of high-quality drawing of rigid optical fiber.

The choice of the system is dictated by the need for using high-temperature glass compositions in order to obtain numerical apertures no lower than 1.05. The synthesized glass



**Fig. 4.** Effect of the chemical composition on the temperature dependence of the logarithm of the viscosity: 1, 4, 7, 10) numbers of the compositions (following Fig. 1) of the experimental glasses for optical-fiber cladding.

compositions are characterized by the absence of crystallization in the formation temperature range, low refractive index ( $n_D = 1.47 - 1.50$ ), high founding temperatures ( $1550 - 1600^\circ C$ ), and a wide formation interval.

The experimental glass compositions have a comparatively low CLTE  $(40 - 80) \times 10^{-7} K^{-1}$ , which is due to the decrease of the decrease of connectedness of the structural network and the appearance in a system of bonds weaker than  $Si - O - Si$  bonds. As the amounts of  $B_2O_3$  and  $SiO_2$  increase the CLTE values decrease to close to  $40 \times 10^{-7} K^{-1}$ .

The viscosity of silicate glasses is due to the strength of the chemical bonds between the particles of the material and the degree of connectedness of the silicon-oxygen framework. As the amount of alkali-metal oxides in the glass increases, the fraction of the non-bridge oxygen atoms increases and, in consequence, the wholeness of the framework decreases and the number of  $Me - O$  bonds ( $Me - Li, Na, K$ ), whose strength is several-fold less than that of  $Si - O$  bonds, increases. The most viscous of the alkali-silicate glasses are potassium-silicate melts [7]. Figure 4 shows curves of the viscosity of the experimental glasses in range  $10^4 - 10^{10} Pa \cdot sec$ .

**TABLE 1.** Comparison of the Main Properties of WY1 and TBF-10 Glasses

Main characteristics of the glasses	WY1	TBF-10
Crystallizability with heat-treatment in the range $650 - 1000^\circ C$ for 6 h	Absence of crystallization	Crystal film with composition $LaTiO_3$ , $Ba_2LaZrO_{5.5}$ , and $La(B_{0.95}SiO_{4.93})$
Light transmission, %	92	92
Refractive index $n_D$	1.7950	1.8206
Average dispersion	0.01926	0.02474
Dispersion coefficient $v_D$	42.97	33.17
Attenuation coefficient, $mm^{-1}$	0.0045	0.0055
CLTE, $10^{-7} K^{-1}$	78.1	77
Density, $10^{-3} kg/m^3$	4.18	4.20
Founding temperature, $^\circ C$	1270	1300



As Fig. 4 shows, replacing  $B_2O_3$  with 5–15%  $K_2O$  (compositions Nos. 7 and 10) shifts the temperature variation of the viscosity curve by 50–70°C to low temperatures. This is due to the weakness of the Me–O bonds.

The replacement of  $B_2O_3$  with 5–15%  $SiO_2$  (compositions Nos. 1 and 10) increases the formation interval and shifts the viscosity curve to high temperatures because the connectedness of the silicon-oxygen network becomes stronger.

A similar relation is observed when  $K_2O$  replaces  $SiO_2$  in the amounts 5–15% (compositions Nos. 1, 4, and 7).

To develop a glass composition with the required temperature variation of the viscosity curve comprehensive use was made of the indicated oxides in the following amounts (%): 7.5–12.5  $K_2O$ , 17.5–22.5  $B_2O_3$ , 70.0–75.0  $SiO_2$ . Of the compositions presented the viscosity of glass No. 4 best meets the viscosity requirements; this glass is characterized by a wide output interval and a shift of the viscosity curve to high temperatures. The glass with composition No. 4 is also characterized by resistance to crystallization in the temperature interval 600–100°C and the required complex of physical-chemical properties and best meets all the conditions for glasses used for light-reflecting cladding. In connection with the fact that the temperature interval of formation of the glass indicated is shifted to high temperatures, its use in production requires a different technological regime for drawing a rigid fiber (temperature, drawing rate, cladding thickness), which predetermines the change of the diameter of the drawn fiber (cladding thickness, light-guide diameter), affecting the volume of the transmitted information. In this connection, at subsequent stages of the work, the optimal composition of  $K_2O$ – $B_2O_3$ – $SiO_2$  glass was modified by oxides of bi- and trivalent elements in order to adjust the viscosity characteristics and maintain the required values of the refractive index and CLTE.

In addition, oxides of the type RO and  $R_2O_3$  are used because of the packing density of the elements of the glass structure, which plays an important role rigid optical fibers are drawn. It is known [5] that the glass structures contain closed voids, which can cause coloring impurities to diffuse from the protective cladding into the light-guiding fiber core. To increase the packing density and prevent diffusion of small-radius ions the composition of glass No. 4 was modified by oxides of bi- and trivalent elements, for which CaO, BaO, and  $Al_2O_3$  were used.

Alkali and alkali-earth metal ions, which have different radii, are distributed over the voids in the network structure and strengthen the glass structure as a whole; in addition, the alkali-earth metal ions increase the degree of connectedness of the network structure and possess higher Me–O bond energy than alkali-metal ions. With regards to the effect on the CLTE in the direction of decreasing its value, alkali-metal ions form the series  $Mg \rightarrow Ca \rightarrow Ba$ . The partial or complete replacement of alkali-metal ions by alkali-earth ions has the opposite effect because of strengthening the

structure as a result of the replacement of alkali cations with low field strength by alkali-earth ions with high field strength. However, the presence in the glass of alkali-metal ions of one type creates an energetically unfavorable packing state [5].

The use of calcium oxide in glasses of this system is justified only in the amounts 0.5–1%, since larger amounts lead to the appearance of opalescence, which under heat-treatment results in volume crystallization.

The use of barium oxide in the experimental glasses is limited to the content 0.5–2.0%; this is because there is a large increase of the refractive index and CLTE. At the same time this oxide makes it possible to decrease the high-temperature viscosity of experimental glasses.

The introduction of  $Al_2O_3$  into a glass composition decreases the CLTE by  $(1.5–2) \times 10^{-7} K^{-1}$ . Its use is justified only in amounts 0.5–2%, because of the large increase in viscosity of the synthesized glasses.

The resistance of the alkali-borosilicate glasses to crystallization increases with added  $Al_2O_3$ . Partial replacement of  $SiO_2$  by  $Al_2O_3$  decreases the liquidus temperature of the glasses and the growth rate of the crystals; this is explained by the capability of aluminum oxide to preserve a high stability of the glassy state. The molar ratio  $Al_2O_3/SiO_2$  is usually maintained in the range 0.1–0.15. It is known [5] that aluminum oxide in silicate glasses also prevents the development of liquation phenomena.

At very high temperatures the melt is mobile and comprises is a system of modifying ions and different fragments of the structural network, which could include different structure-forming units and groupings. If the size of a modifying ion is greater than that of the internal voids, which exist in the network of the initial glass-forming oxide, then the newly formed network will contain a number of voids which are larger than the voids present in a network with no modifying ions. However, if the modifying ions are small, their attraction to the oxygen ions can decrease the size of the voids. For this reason, when the compositions of experimental glasses are modified, metal oxides with a small ionic radius should be added.

It has been established experimentally that the optimal results were obtained by introducing aluminum potassium, and barium oxides in the amounts indicated above.

The glass composition obtained for light-reflecting cladding possesses a complex of the required properties: resistance to crystallization in the temperature interval 800–1000°C, refractive index  $n_D = 1.49$ , CLTE equal to  $68 \times 10^{-7} K^{-1}$ , and the required formation interval.

The protective (colored) cladding serves to prevent undesirable entry of light from the light-reflecting cladding into the neighboring light-guide or into the surrounding medium. Glass for the protective cladding is required to meet conditions with respect to the magnitude of the CLTE, the optical density, and the temperature behavior of the viscosity curve.

**TABLE 2.** Twister Properties

Twister properties	Twister	
	developed	commercial
Aperture of article $A = \sqrt{n_{D1}^2 - n_{D2}^2}$	1.03	1.05
Light transmission $\tau_{550}$ , %:		
at thickness 5 mm	57	53
at thickness 15 mm	48	45
Contrast transmission coefficient (CTC), $\text{mm}^{-1}$	—	0.99
CLTE difference between the light-transmitting core glass and the light-reflecting cladding, $\text{K}^{-1}$	$9 \times 10^{-7}$	$22 \times 10^{-7}$

Optimization of the glasses used for the light-guiding fiber core and for the cladding made it necessary to adjust the composition of the glass for the protective cladding (VTO-73) with respect to the viscosity properties.

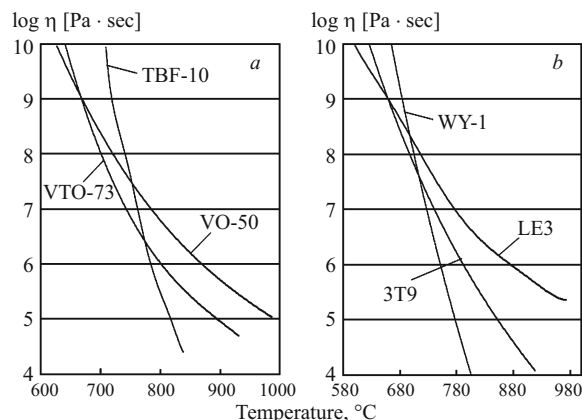
In this connection, a series of experimental glasses based on the system  $\text{Na}_2\text{O} - \text{K}_2\text{O} - \text{CaO} - \text{MgO} - \text{BaO} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$  with the following content limits (%) was synthesized: 60–80  $\text{SiO}_2$ , 5–25  $\text{B}_2\text{O}_3$ , and 10–30  $\text{Na}_2\text{O}$ ; the content of the oxides  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{BaO}$  was constant and equal to 10%. Coloring agents, which give the required optical density and contrast, are added to the composition of the glass used for the protective cladding. The oxides  $\text{CoO}$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Mn}_2\text{O}_3$  were used as coloring agents; their mass content was 0.4–0.45%, introduced above 100%.

The synthesized glasses are resistant to a phase transition in the temperature interval 600–1000°C and have high CLTE —  $(45 - 115) \times 10^{-7} \text{ K}^{-1}$ . The high CLTE values are due to additions of sodium oxide, which decreases the degree of connectedness of the structural network; boron oxide gives minimal values.

Just as for the light-reflecting cladding,  $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  added in place of  $\text{SiO}_2$  in amounts 5–20% shift the temperature curve of the viscosity by 100°C to low temperatures; this is due to the weakness of the  $\text{Me} - \text{O}$  bonds.

The composition of glass for the protective cladding of a rigid optical glass fiber with the required technological and physical-chemical properties was obtained from studies of the dependence of the chemical composition on the viscosity in the range  $10^{10} - 10^4 \text{ Pa} \cdot \text{sec}$ .

To prevent coloring oxides from entering the glass of the light-guiding fiber core while preserving the required optical density, studies were performed to determine the effect of the concentration and type colorants on the degree of their diffusion. It was found that the most easily diffusing colorant is cobalt oxide, but the required degree of contrast of the finished product limits the amount by which cobalt oxide can be decreased; the optimal mass content of  $\text{CoO}$  is 0.2–0.25%.



**Fig. 5.** Comparison of the temperature dependence of the logarithm of the viscosity of commercial (a) and developed (b) glass compositions for obtaining a rigid optical fiber.

A twister possessing the complex of properties presented in Table 2 was fabricated from the three glasses obtained with optimal composition and matched refractive index and CLTE.

As Table 2 shows, the twister developed is characterized by high light transmission and minimal difference of the CLTE between the fiber core and the cladding, which gives a high volume of transmitted information and the required thermomechanical strength of the finished article. In addition, the glasses for twisters were picked according to the rheological properties so that twisters can be obtained at 620–630°C without any visible indications of deformation of the light guides (Fig. 5).

In summary, the development of the glass compositions for a rigid optical glass fiber permits matching all three glasses with respect to the index of refraction, the CLTE, the temperature dependence of the viscosity, and the absence of any indications of phase separation. The glass compositions developed can be used to manufacture fiber-optic articles.

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